

Fluoropolymers for 157nm Lithography: Optical Properties from VUV Absorbance and Ellipsometry Measurements

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ABSTRACT

With the introduction of 157 nm as the next optical lithography wavelength, the need for new pellicle and photoresist materials optimized for this wavelength has produced much activity in optical characterization of thin film materials. Here we focus on ultratransparent fluoropolymers for 157 nm pellicle applications where absorbances below 0.01/ μm are necessary to achieve transmissions above 98%. Transmission-based absorbance/ μm measurements performed using VUV spectroscopy are characterized by rapid turn-around time, and are essential during the materials design and screening phase of a new materials development program. Once suitable candidate materials families have been identified for development into 157 nm pellicles, VUV ellipsometry becomes essential to model the film structure, characterize the complex index of refraction, and to tune the pellicle's etalon design.

Comparison of VUV absorbance measurements of fluoropolymer thin films on CaF_2 substrates with VUV ellipsometry measurements of the same polymers on silicon substrates demonstrates some of the artifacts in, and helps define the accuracy of transmission based absorbance measurements. Fresnel interference fringes can produce transmission oscillations that can lead to underestimation, or even negative values, of the film absorbance. Film thickness nonuniformity can serve to reduce the Fresnel interference fringes, leading to reduced variation in the apparent 157 nm absorbance for μm thick films. VUV ellipsometry coupled with Fresnel analysis of the thin film/substrate system formally takes into consideration all of these optical artifacts, while at the same time determining the complex index of refraction of the materials. Using VUV ellipsometry and Fresnel analysis, the absorbance values do not show the large apparent oscillations, the film thickness is directly determined in the measurement, and film microstructure is also modeled.

We have identified ultratransparent fluoropolymers which have 157 nm absorbances below 0.01/ μm . These materials have the appropriate optical properties for use as 157 nm pellicles with greater than 98% transmission. This is an important for the development of 157 nm lithography, since the lack of a 157nm pellicle has been identified as a critical path issue.

Keywords: pellicles, 157 nm lithography, fluoropolymers, vacuum ultraviolet, VUV spectroscopy, VUV ellipsometry

1. INTRODUCTION

With the introduction of 157 nm as the next lithographic wavelength, activity has been initiated¹ to develop the materials needed for optical steppers, lenses, coatings^{2,3}, photomasks, pellicles, and photoresists⁴. Much of this type of work began at 248 nm and 193nm, where the high energy of the illumination introduced new issues and problems. Solutions developed include chemically amplified resists, new laser illuminators, the introduction of optical scanners, and new fluoropolymers for pellicle applications⁵. Use of 157 nm (7.9 eV) radiation poses new problems. Few materials, either inorganic or organic are known to have significant transmission at this vacuum ultraviolet (VUV) wavelength. In addition, such high energy radiation can introduce new radiation damage mechanisms in previously accepted optical materials.

For 157 nm pellicles, new ultratransparent materials are required to achieve the goal transparency of 98% at the lithographic wavelength. Development of these new materials requires detailed understanding of the optical measurement instruments and analysis. In this paper, we compare VUV absorbance measurements of fluoropolymer thin films on CaF_2 substrates with VUV ellipsometry measurements of these polymers on silicon substrates.

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Materials Design for Lithographic Pellicles

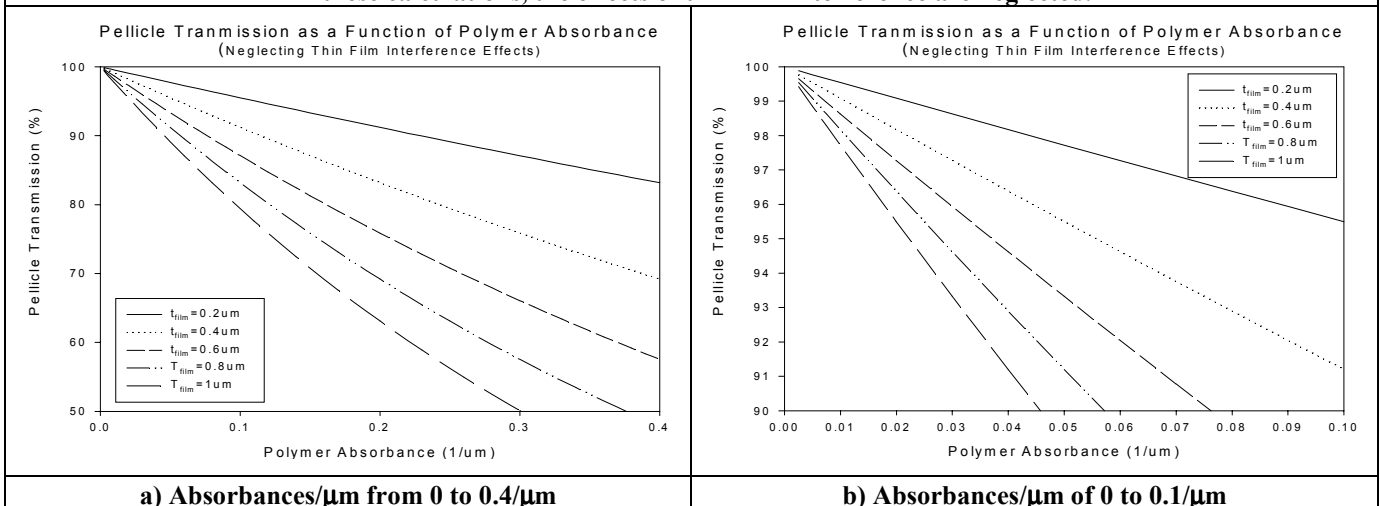
The pellicle is a critical component for successful photolithography. In an optical stepper, the pellicle serves as a contamination control device. The pellicle consists of a precisely designed membrane, which acts as a tuned etalon,⁶ on a pellicle frame that is adhesively mounted to the reticle or photomask. If a particulate contaminant deposits onto the reticle, it will be kept out of the image plane of the reticle and therefore will be out of focus. Pellicles reduce contamination, but introducing any optical element into the complex and precise imaging of a photolithographic stepper or scanner demands careful consideration of the optical effects. Beyond the optics of the pellicle, pellicles also have a large number of ancillary properties that are essential.

The multiple property requirements embodied in pellicles require a materials design approach. Currently, no materials are known to meet the optical transparency performance requirements at the 157 nm lithography wavelength. The use of new materials requires that careful attention be given to design of the tuned etalon to control the pellicle reflectance and transmission. To achieve the desired pellicle lifetimes, new radiation tolerant materials will need to be developed that meet stringent radiation durability requirements. To produce unsupported pellicle membranes, the polymer must also be designed to achieve the required spinning, film formation, and mechanical properties, and have minimal outgassing in use.

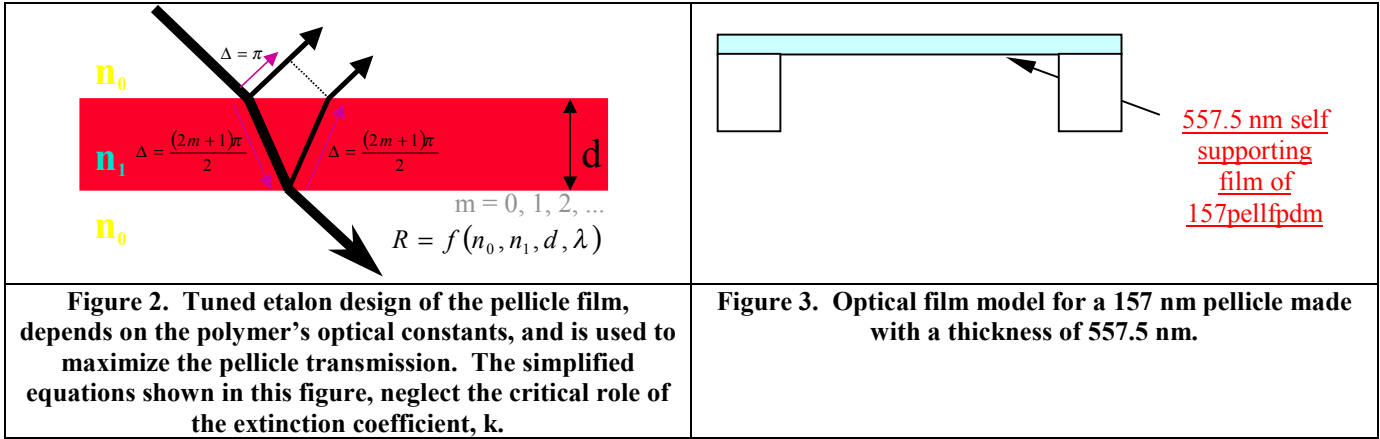
Optical Designs and Requirements for 157 nm Pellicles

Since it is known that current commercial fluoropolymers do not exhibit the goal transmissions of greater than 98% transmission at 157 nm, it is instructive to look at 157 nm pellicle designs to determine the target optical properties. To determine the necessary optical absorbance (discussed in detail in Section 2) we first consider the optical transmission of pellicle films of differing thicknesses, while neglecting the effects of the thin film, or Fresnel, interference.⁶ These results are shown in Figure 1a for polymers with an absorbance at 157 nm from 0 to 0.4/ μm . For reference, typical polymers have absorbances/ μm which range up to 20/ μm . Commercial TeflonAF[®] fluoropolymer has an absorbance of 0.42/ μm while Cytop[®] has an absorbance of 1.76/ μm . For film thicknesses on the order of 0.8 μm , we see that pellicle transmissions using these materials approach 50%, much below the 98% transmission goal. In Figure 1b we consider the much lower absorbance/ μm range, 0 to 0.1/ μm . Here we see that for comparable film thicknesses, we need an absorbances/ μm of less than 0.02, 20 times lower absorption than that of TeflonAF[®], the clearest commercial fluoropolymer.

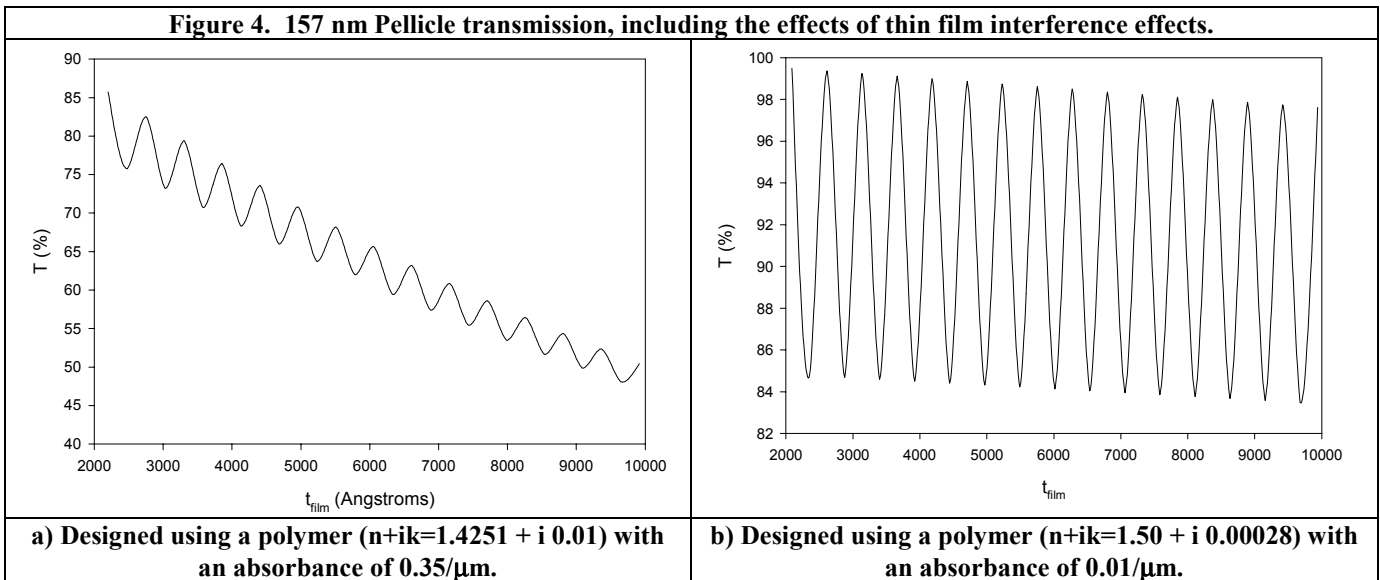
Figure 1. 157 nm Pellicle transmission as a function of polymer absorbance/ μm for pellicle films of various thickness. In these calculations, the effects of thin film interference are neglected.



Consideration of the effects of the Fresnel interference is essential in pellicle design since it can lead to large changes in the reflection and transmission of both pellicle and supported film samples. To optimize the pellicle design, we tune the etalon (as shown in Figure 2) to determine the Fresnel fringes and evaluate the achievable pellicle transmission. The optical film model we use is shown in Figure 3. Specifically we consider an unsupported 157 nm pellicle polymer (157pellfpm) with a thickness of 557.5 nm.



We systematically vary the pellicle film thickness and calculate the pellicle transmission, Figure 4, for two different polymers, one with an absorbance of 0.35/μm and one with an absorbance of 0.01/μm. For these pellicles designs one can see the transmission swings of the tuned etalon design. These minima and maxima in the pellicle transmission as a function of the film thickness arise from coherent interference of the front and back side reflections at the polymer/air interfaces. For pellicles designed from a polymer with an absorbance of 0.35/μm (Figure 4a) the transmission does not approach 90% even from films as thin as 200 nm. One can see, therefore, that one strategy for increasing the transmission of a 157 nm pellicle is to make the pellicle film thinner. This will reduce the attenuation of the light by the pellicle, but will place very difficult demands on the mechanical properties of the material. In addition, it also increases the sensitivity of the materials and processing to defects that may result in pinholes.



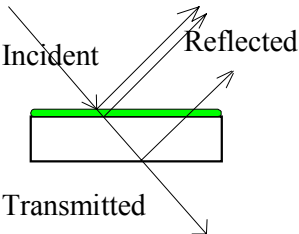
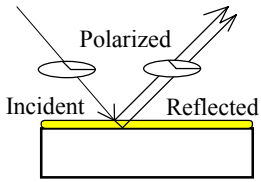
Instead, if one can develop ultratransparent 157 nm polymers with an absorbance of < 0.01/μm, films with thicknesses up to 700 nm can be used that achieve transmissions > 98%, if properly tuned. A tuned etalon design for a 157 nm pellicle made from a polymer with an absorbance of 0.01/μm is shown in Figure 4b.

2. EXPERIMENTAL AND ANALYTICAL TECHNIQUES

Optical Characterization for 157 nm Pellicle Materials Design

Development of new materials for use in 157nm photolithography will involve both VUV spectroscopy and VUV spectroscopic ellipsometry. This is because the required transparency of the pellicle film is high, and the accuracy of simple transmission based absorbance/μm measurements (Figure 5) is insufficient. Instead, ellipsometry based (Figure 6) film

structure and optical models are required to determine the complex index of refraction and the film thicknesses. Also, the rapid turn around time possible from absorbance measurements is essential in the materials screening phase, as novel materials are being developed.

	
<p>Figure 5. Schematic of VUV spectroscopy measurement of spectral transmission or reflection.</p>	<p>Figure 6. Schematic of VUV ellipsometry measurement of polarized reflectance.</p>

Sample preparation

Polymer films were prepared by spinning from solution onto various substrates. For VUV spectroscopy, CaF₂ substrates from Bicon⁷ and Optovac⁸ were used, while for VUV ellipsometry, films were deposited on silicon wafers. Film thicknesses were measured using a Filmetrics⁹ F20 thin film measurement system.

Vacuum Ultraviolet Spectroscopy

VUV spectroscopy including both transmission and reflectance measurements has become an established technique for electronic structure studies of large band-gap, insulating materials such as polysilanes¹⁰ and fluoropolymers. It has the advantage of covering the complete energy range of the valence interband transitions, therefore supplying insight into the interatomic bonds producing absorptions¹¹. The details of the VUV-LPLS spectrophotometer have been discussed previously.¹² The spectrophotometer is shown in Figure 7 and utilizes a laser plasma light source (LPLS),¹³ and a 1 meter monochromator with Al/MgF₂ and iridium coated optics. The energy range of this windowless instrument is 1.7 to 44 eV (700 to 28 nm), which extends beyond the air-cutoff of 6 eV and the window-cutoff of 10 eV. The resolution of the instrument is 0.2 to 0.6 nm, which corresponds to 16 meV resolution at 10 eV and 200 meV resolution at 35 eV.

A Perkin Elmer Lambda 9 spectrophotometer, with transmission and reflectance attachments and using xenon and deuterium lamps, was used to cover the UV/vis/NIR spectral regions. The wavelength (energy) resolution is 2 nm (40 meV) at 5.0 eV. Transmission was measured over the complete energy range of the instrument to check the accuracy of the VUV transmission spectra. The results agreed well with the data from the VUV spectrophotometers. Data were spliced together in the overlapping wavelength region using a multiplicative scaling factor on the VUV transmission to bring it into agreement with the UV/vis results.

Absorbance/ μm From Transmission Based Vacuum Ultraviolet Spectroscopy

Once the transmission spectra of the substrate and the film coated on that substrate are determined, the film transmission and optical density can be determined using Equation 1 and Equation 2 respectively. The absorbance/ μm ($A/\mu\text{m}$) is then determined by dividing the optical density by the film thickness, as shown in Equation 3.

$$\text{Equation 1.} \quad T_{film} = 100 \frac{T_{sample}}{T_{substrate}}$$

$$\text{Equation 2.} \quad O.D._{film} = \text{Log}_{10} \frac{100}{T_{film}}$$

$$\text{Equation 3.} \quad A_{film} (\mu\text{m}^{-1}) = A / \mu\text{m} = \frac{\text{Log}_{10} [T_{substrate} / T_{sample}]}{t_{film}}$$

Vacuum Ultraviolet Spectroscopic Ellipsometry

The variable angle spectroscopic ellipsometry measurements were taken on the Woollam Co.¹⁴ VUV-VASE™, shown in Figure 8.¹⁵ It covers the wavelength range from 142nm to 1700nm with an angle range from 15° to 90°. It is based on a rotating analyzer VASE® instrument, which covers the UV-Visible-NIR spectral range. It incorporates a computer controlled MgF₂ Berek waveplate as a compensator to improve the ellipsometric Δ measurement accuracy. The introduction of a retarding element also allows the ellipsometer to distinguish unpolarized light. This was found to improve results when dealing with thicker films, because it allowed a careful treatment of non-idealities such as instrument bandwidth and sample non-uniformity. The entire system is purged with dry nitrogen gas to avoid absorption of VUV light by ambient oxygen and water vapor. Light from both the deuterium lamp and the xenon lamp passes through a double-chamber Czerny-Turner type monochromator to provide wavelength selection and stray-light rejection. Computer-controlled slit widths can adjust the bandwidth to insure adequate spectral resolution of optical features in the data such as the closely spaced fringes, which arise in very thick films. A photomultiplier tube is utilized for signal detection in the ultraviolet. A stacked Si/InGaAs photodiode detector is used for longer wavelengths.

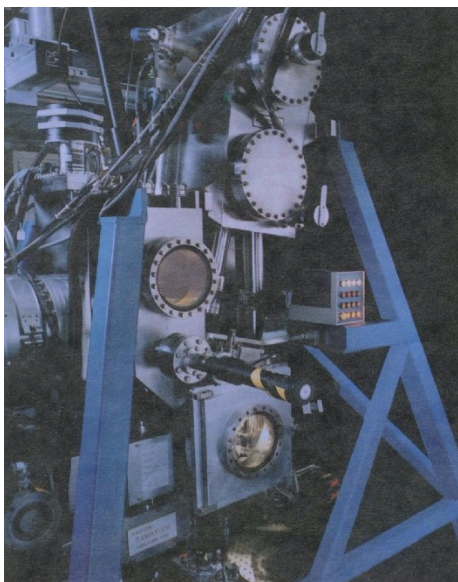


Figure 7. VUV-LPLS spectrophotometer.

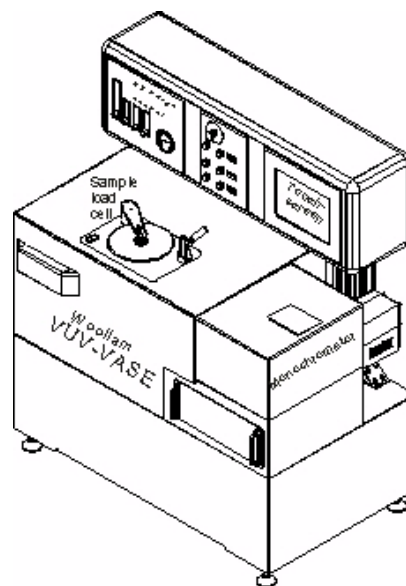


Figure 8. VUV-VASE spectroscopic ellipsometer.

Optical Properties from Vacuum Ultraviolet Spectroscopic Ellipsometry

The ellipsometry data was “fit” to determine the polymer film thickness and complex refractive index (Equation 4).¹⁶ A parameterized model was used to describe the polymer optical constants over the wide spectral range. This enabled the calculation of the complex refractive index as a function of wavelength with a much smaller set of free parameters. We chose the Tauc-Lorentz model¹⁷ for these films, which remains Kramers-Kronig consistent and helps describe the onset of film absorption.

Because the optical absorption of the film is important, μm thick films were measured instead of the 200 nm thick films typically studied in ellipsometry. This increases the path length of light through the material, which improves sensitivity to small values of the extinction coefficient k . However, thicker films are more susceptible to the effects of non-uniformity and finite spectrometer bandwidth. Ellipsometers that include a retarding element are capable of measuring % depolarization.¹⁸ Both non-uniformity and finite-bandwidth can depolarize the measurement beam. We quantify these non-ideal effects and model their behavior during analysis of the experimental data. In this manner, the optical constants can be determined with a higher degree of certainty.

$$\text{Equation 4.} \quad \hat{n} = n + ik$$

Once the extinction coefficient k has been determined, the optical absorption parameters α and A can be determined using Equation 5, or for values appropriate for 157 nm, Equation 6. The absorption coefficient, α , corresponds to the attenuation of the light transmitted through the sample calculated on a natural logarithm basis. Since the absorbance per μm ,

A, is determined from the base 10 logarithm of the optical density given in Equation 2, a value of $\ln(10)$ or 2.302585 is introduced into Equation 5. Both k and α are inherent optical properties of the material. On the other hand, absorbance/ μm is frequently based only on transmission measurements, and thus neglects effects arising from the index mismatch between the film and substrate, thin film (or Fresnel) interference effects, and film nonuniformity effects.

$$\text{Equation 5.} \quad k = \frac{\alpha\lambda}{4\pi} = \ln(10) \frac{A\lambda}{4\pi} = 2.302585 \frac{A\lambda}{4\pi}$$

$$\text{Equation 6.} \quad \text{Abs.}(157\text{nm}) = 34.761 k(157\text{nm})$$

3. RESULTS AND DISCUSSION

Optical Properties and Absorbance/ μm of Ultratransparent Polymers for 157 nm Pellicles

VUV absorbance/ μm measurements of three experimental Teflon AF[®] polymers, denoted TAFx23, TAFx24 and TAFx25 are presented in Table 1. Table 2 shows the results from VUV ellipsometry measurements. For the absorbance/ μm results, film thickness, substrate and sample transmission are presented along with the ΔT ($=T_{\text{substrate}} - T_{\text{sample}}$) values. Positive values of ΔT correspond to an increase in the samples transmission compared to the bare substrate and result in an apparent negative absorbance/ μm . This is the result of an interference effect similar to that of an antireflective coating arising from the presence of the thin polymer film with an index of refraction lower than that of the substrate. The variability in the CaF₂ substrates is shown in Figure 9, where the as-received substrate transmissions are summarized. Substantial variations in transmission have been noted for substrates coming from different sources and batches. This is the result of impurity absorptions, and possibly the result of surface contamination. The ellipsometry results table shows film thickness, the complex index of refraction of the polymer films and the absorbance/ μm calculated using the extinction coefficient determined by applying Equation 5.

Table 1. VUV Spectroscopy Measurements on Selected TAFx Polymers						
Exp. #	Polymer	Thickness (μm)	T _{substrate} (%)	T _{sample} (%)	ΔT (%)	157 nm Absorbance/ μm
1	TAFx23	2.824	83.95	83.88	-0.07	0.005
2	TAFx23	2.267	84.68	82.55	-1.03	0.00012
3	TAFx23	1.803	82.23	80.50	-1.73	0.005
4	TAFx23	1.803	84.20	80.07	-4.13	0.012
5	TAFx23	0.963	71.18	72.12	0.93	-0.005
6	TAFx23	0.864	83.50	85.15	1.65	-0.01
7	TAFx23	0.451	83.65	82.98	-0.7	0.008
8	TAFx23	0.287	82.82	81.43	-1.38	0.016
Avg.		1.408				0.0059
9	TAFx24	3.710	74.00	5.67	-68.32	0.30
10	TAFx24	1.281	79.99	16.67	-63.24	0.386
Avg.		2.500				0.343
11	TAFx25	2.177	86.10	78.62	-7.49	0.017
12	TAFx25	1.276	79.64	74.94	-4.70	0.021
Avg.		1.727				0.019

TAFx23, which has an absorbance below 0.016/ μm , was the most extensively studied fluoropolymer, with eight absorbance and two ellipsometric measurements. This novel fluoropolymer falls in the range of absorbances necessary to achieve 157nm pellicle transmissions of 98%. The range in VUV absorbance values (shown in Figure 10) extends from 0.016/ μm to -0.01/ μm . The origin of this variability will be discussed below. The ellipsometric values of the absorbance/ μm are in much closer agreement, ranging from 0.0074 to 0.0082/ μm , demonstrating the greater accuracy of the

ellipsometric measurement and modeling and confirming that this polymer is capable of producing high transparency in a 157 nm pellicles.

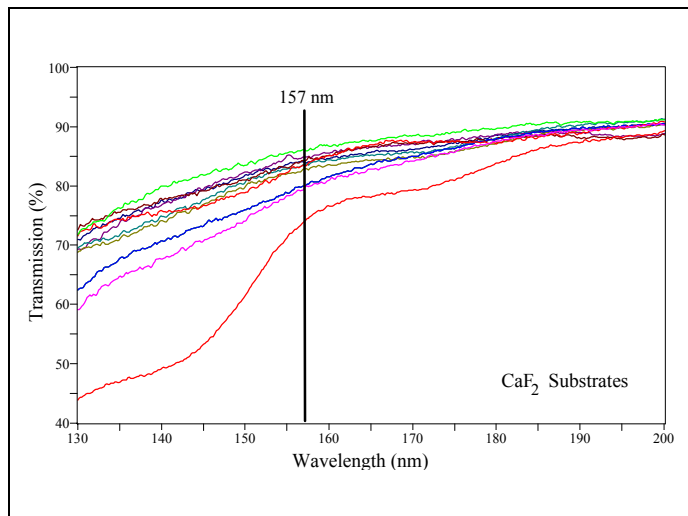


Figure 9. Variability of the spectral transmission of CaF₂ substrates.

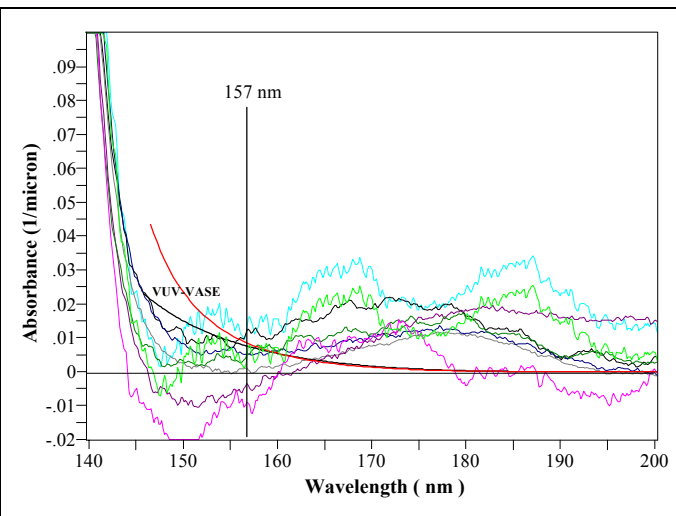


Figure 10. Spectral absorbance/μm for TAFx23, determined from VUV spectroscopy and ellipsometry. Thick lines represent results from VUV-VASE. Thin lines show results from VUV spectroscopy.

Table 2. VUV Ellipsometry Measurements on Selected TAFx Polymers					
Exp. #	Polymer	Thickness (μm)	Index of Refraction n	Extinction Coefficient k	157 nm Absorbance/μm
13	TAFx23	1.399	1.4913	0.00021	0.0074
14	TAFx23	0.955	1.4928	0.00024	0.0082
Avg.		1.177	1.492	0.00023	0.0078
15	TAFx24	1.380	1.6059	0.01017	0.35
16	TAFx25	1.243	1.4441	0.0001	0.0033

The absorbance spectra of TAFx24 presented in Figure 11 shows that it is more strongly absorbing (0.35/μm) than the ultratransparent TAFx23 and TAFx25 fluoropolymers. There is close agreement between the results of VUV absorbance and ellipsometry measurements. One must note the saturation of the absorbance spectra below approximately 150 to 153 nm, which arises from the saturation of the transmission measurement. This can also be seen by the very large ΔT values for these measurements.

TAFx25 is the second ultratransparent 157 nm polymer presented here. The absorbance curves, Figure 12, shows it to have an absorbance of less than 0.02/μm at 157 nm. In this case, the absorbance measurements suggest the presence of some absorption centered around 175nm, while the ellipsometric results do not show this. If there is a true absorption in the material, then it will not be observed in the ellipsometry results as modeled here due to the parametric optical constant model chosen which does not contain absorption peaks below the fundamental band gap of the material. A refinement of the parametric optical constant model could have been used to model this apparent 175nm absorption peak.

Comparing the absorbance/μm of TAFx23 and TAFx25 with the pellicle designs in Section 1, it is pleasing to see that both VUV spectroscopy and ellipsometry confirm that these two polymers have the appropriate optical properties for use as 157 nm pellicles with greater than 98% transmission. This is an important finding for 157 nm lithography, since the lack of an 157 nm pellicle has been identified as a critical path issue.

VUV Spectroscopy and VUV Ellipsometry for Materials Screening and Development

Transmission based absorbance/μm measurements performed using VUV spectroscopy are characterized by rapid turn around time, and are essential during the materials design and screening phase of a new materials development program.

However, the substantial limitations, approximations, and complete neglect of important optical effects in the analysis of the transmission data to determine the absorbance/ μm is a major limitation. To properly apply absorbance/ μm measurements, careful consideration must be given to the experimental and analytical artifacts that may arise.

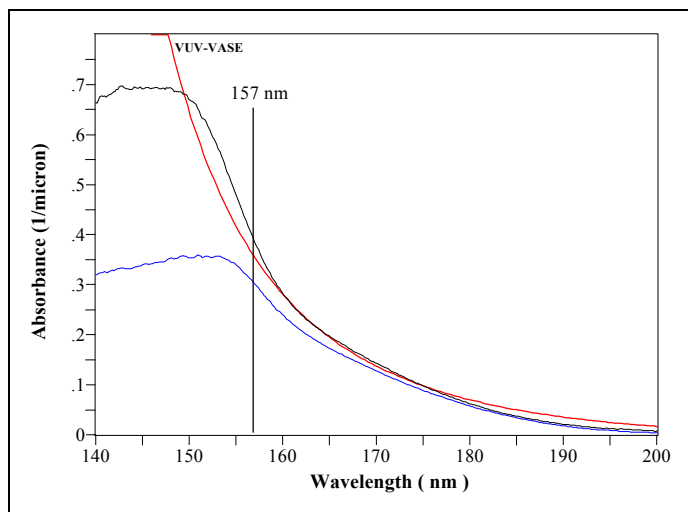


Figure 11. Spectral absorbance/ μm of TAFx24. Below 150 to 153 nm, saturation of the measurement is evidenced by the plateau in the absorbance. The thick line represents results from VUV-VASE. The two thin lines show results from two different samples as measured by VUV spectroscopy.

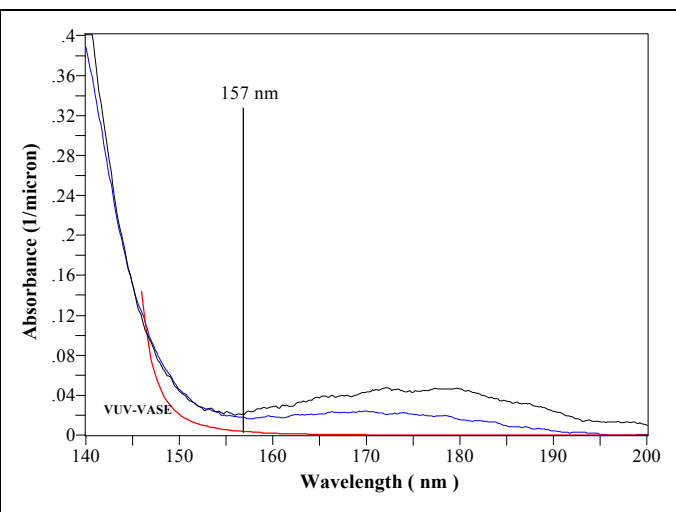


Figure 12. Spectral absorbance/ μm of TAFx25. The thick line represents results from VUV-VASE. The two thin lines show results from two different samples as measured by VUV spectroscopy.

Once suitable candidate materials families have been identified for development into 157 nm pellicles, VUV ellipsometry becomes essential for the measurement of the index of refraction and the extinction coefficient of the materials, and to model the film structure. This detailed optical and film microstructure analysis is required for the tuned etalon design. The optical properties can be determined using combined transmission and reflection measurements and Fresnel analysis, but the inherently increased sensitivity and accuracy of the polarization dependent data and ratio measurements from ellipsometry make ellipsometry the preferred method.

Experimental Variability Arising in Absorbance/ μm Measurements

VUV spectroscopy requires the accurate measurement of transmitted light intensities, and has inherent limitations in terms of accuracy and reproducibility. The use of dual beam spectrometers such as the Perkin Elmer Lambda19 has improved accuracy and reproducibility when compared to the single beam VUV LPLS spectrophotometer. But both types of instrument rely on the equivalence of optical elements and detectors in multiple optical paths, and/or the stability of the instrument over time. These assumptions can be reasonable in the traditional UV/vis/NIR/FTIR spectral regions, but in the VUV such assumptions can be inadequate. Since transmission based absorbance/ μm measurements result directly from the difference in transmission, ΔT , of the substrate and the film on the substrate, the accuracy to which ΔT can be known is a major limitation. In these ultratransparent polymers, the film transmission is on the order of 100% and ΔT is close to zero as shown in Table 1.

Transmission based measurements also require that the film thickness of the sample on the substrate be optimized for the dynamic range of the spectrophotometer so that the transmittance of the film and substrate falls in the range from 3 to 90%. If the transmittance falls much below 1%, the accuracy of the measurement is severely degraded and erroneous results appear. This can be seen in Figure 11, which shows ellipsometric results and transmission measurements for two different TAFx24 films. The film thickness of $\sim 2.5 \mu\text{m}$ combined with the materials absorbance of $0.03/\mu\text{m}$ result in such low transmitted light intensity below a wavelength of 150 nm that the resulting absorbance values are essentially meaningless.

In addition to the variability in the measurements, the quality of the CaF_2 substrates is highly variable due to bulk absorptions and surface contamination issues. These issues are more critical at 157 nm than at longer wavelengths, since materials are much more strongly absorbing at 157 nm. This variability requires that each substrate be measured before the thin film is deposited and then used in calculation of the film's absorbance/ μm calculations. In more well established optical

materials such as ultrahigh purity fused silica or single crystal sapphire, the assumption that the substrates are all comparable is an acceptable approximation. For substrates of CaF_2 , transmission variability range from 86 to 71%.

Knowledge of the film thickness is also required to determine the absorbance/ μm . Determination of the thickness of a soft polymer film which is nearly index matched to a transparent substrate can be very challenging. This thickness uncertainty enters directly into the accuracy of the resulting absorbance/ μm values.

Optical Artifacts Arising in Transmission Based Absorbance/ μm Determination

Transmission based absorbance/ μm measurements rely on a series of assumptions and approximations. Typically, artifacts arising from the index mismatch between the film and substrate, thin film (or Fresnel) interference effects, and film nonuniformity effects are ignored. To quantify the magnitude and impact of these approximations for ultratransparent polymers intended for 157 nm pellicles, we calculate the optical performance of a model system with realistic optical constants with full consideration given to effects of index of refraction, Fresnel interference, and thickness nonuniformity. This then helps us to quantify the impact of the above mentioned approximations.

Let us consider the model system, shown in Figure 13 that consists of a thin polymer film on a CaF_2 substrate. In this case we choose the polymer to be an appropriate ultratransparent polymer, such as TAFx23. We will use predetermined optical properties for the TAFx23 polymer of $n+ik=1.493 + i 0.00023708$. This corresponds to a film Absorbance of $0.0082/\mu\text{m}$. The model also assumes 1mm thick CaF_2 substrate with $n+ik = 1.5912+i 0$. Note that since we know a priori the absorbance of the polymer film in this model system, the absorbance calculated from the sample transmissions will serve to quantify the inaccuracies or artifacts in transmission based absorbance/ μm measurements.

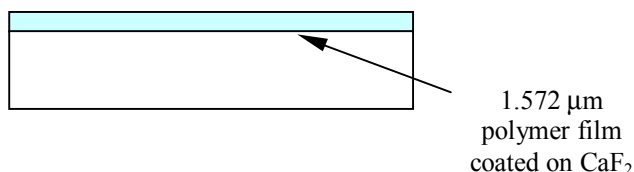
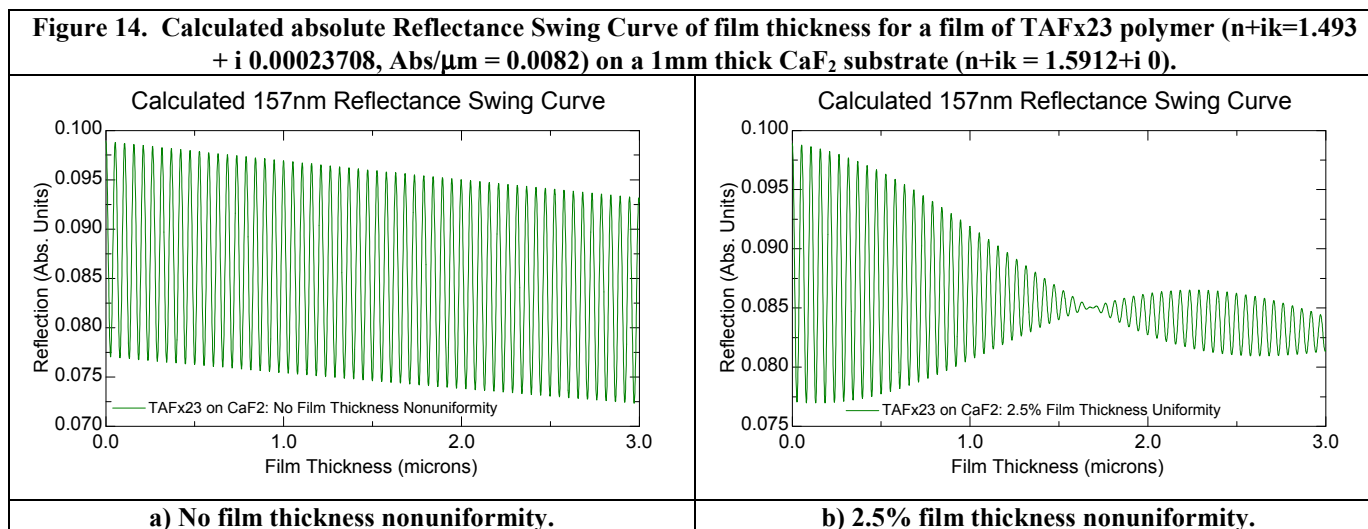


Figure 13. An optical model of a thin polymer film of TAFx23 on a CaF_2 substrate appropriate for transmission based Absorbance/ μm measurements. The absorbance of this polymer is $0.0082/\mu\text{m}$.



At 157 nm the polymer has an index of refraction which is intermediate between that of the CaF_2 substrate and air. It therefore serves as an antireflective (AR) coating on the substrate, reducing the reflected light, and thereby increasing the optical transmission of the polymer coated substrate. This can be seen in Figure 14a where the bare CaF_2 substrate has $\sim 9.5\%$ reflectivity and with the addition of very thin polymer film causes the reflectance to drop to $\sim 7.5\%$. The reflectance decrease caused by very small polymer film thicknesses leads to an increase in the transmission of the sample from 90.1% to $\sim 92\%$ as is shown in Figure 15a. This increase in the transmission of the film and substrate relative to the substrate alone,

will produce negative values of the absorbance/ μm when calculated using Equation 3. One should also note that these reflectance and transmission swings are larger than many of the ΔT values reported in Table 1.

Beyond this simple AR coating effect, the polymer film exhibits Fresnel interference fringes that modulate the reflectance and transmission of the film as the thickness is varied. These lead to the reflectance swing curves shown in Figure 14a and their related transmission swing curves shown in Figure 15a and result in variations of the reflectance and transmission on the order of 2.5%. Since Equation 3 has the absorbance/ μm scaling with the ratio of $T_{\text{substrate}}$ to T_{sample} , then the Fresnel interference fringes will produce oscillations in the reported absorbance values. This effect will be reduced for polymers with appreciable values of the extinction coefficient or absorbance, since it will tend to damp the interference fringes.

Figure 15. Calculated absolute transmission swing curves for a film of TAFx23 polymer ($n+ik=1.4928 + i 0.00023708$, $\text{Abs}/\mu\text{m} = -0.00824$) on a 1mm thick CaF2 substrate ($n+ik = 1.5912+i 0$, substrate transmission of 90.1%).

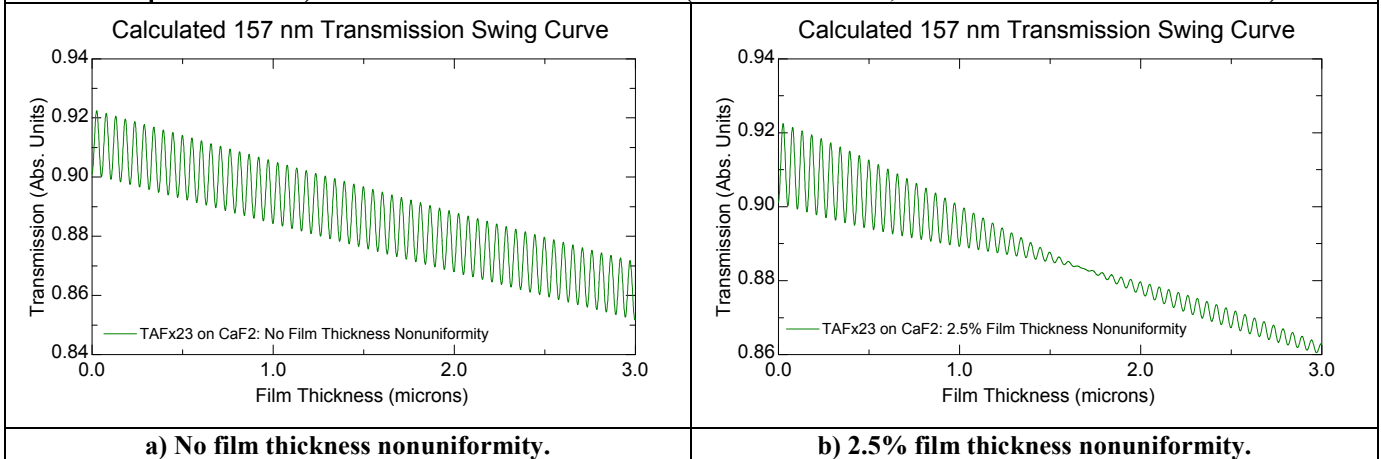
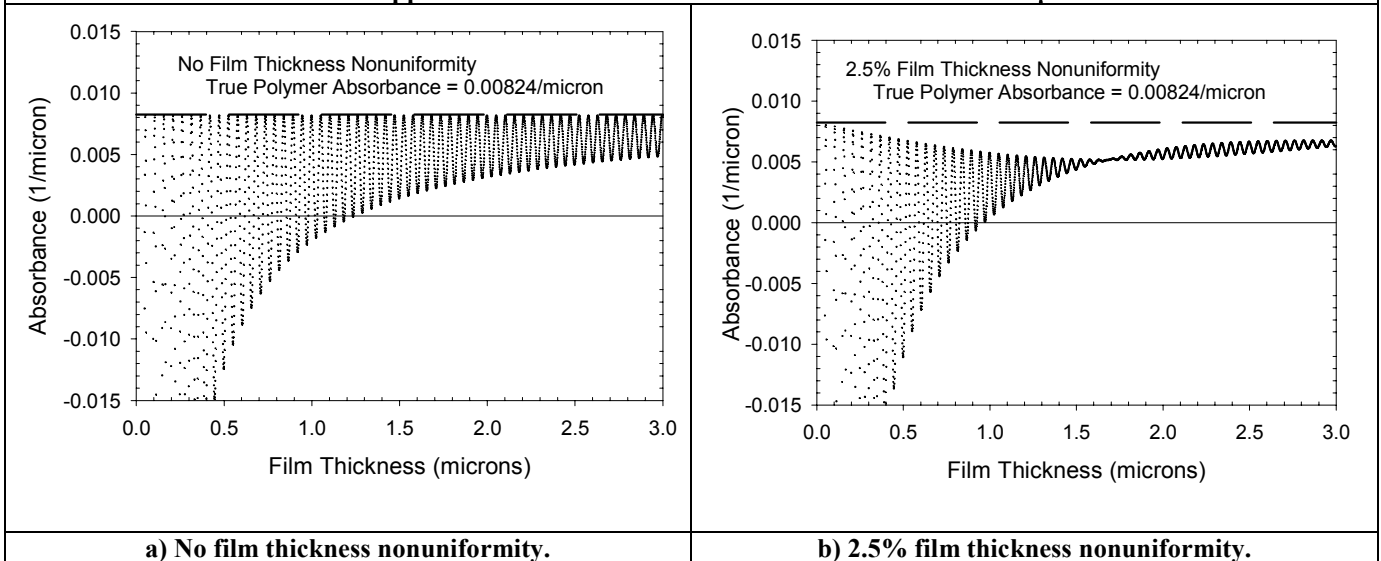


Figure 16. The absorbance/ μm calculated from a film of TAFx23 polymer ($n+ik=1.4928 + i 0.00023708$, $\text{Abs}/\mu\text{m} = -0.00824$) on a 1mm thick CaF2 substrate ($n+ik = 1.5912+i 0$, substrate transmission of 90.1%). Absorbance calculation errors approach a maximum of -0.44 for a film thickness of $0.02 \mu\text{m}$.



For ultratransparent materials, such as those studied here, the very low absorbance requires that films of appreciable thickness be measured, so that enough absorption occurs in the polymer film to produce a measurable value of ΔT . If the polymer film has no film thickness nonuniformity, the Fresnel interference fringes produced are present for films of any thickness. In realistic films, film thickness nonuniformity is present and will scale with the thickness of the film. From our spectroscopic ellipsometry modeling, we found a film thickness nonuniformity on the order of 2.5% for these small scale

research samples. This film thickness nonuniformity plays a very useful role in the optical measurements, since with increasing film thickness the Fresnel interference fringes suffer destructive interference and are dramatically damped. These results are shown in Figure 14b for the reflectance swing curves and in Figure 15b for the transmission swing curves. These tend to show a dramatic reduction in the interference fringes for film thicknesses of approximately 1.5 μm , which is in the target film thickness range used in this study.

Let us now take the transmission swing curves presented in Figure 15 and use them as input data for the calculation of the absorbance/ μm from this model polymer film on CaF_2 substrate. The polymer film material used in this model calculation has an absorbance of 0.0082/ μm . We plot the calculated absorbance/ μm for this model system in Figure 16a for the case of no film thickness nonuniformity and in Figure 16b for 2.5% film thickness nonuniformity. Here we see that, for film thicknesses below 0.5 μm , the AR coating effect and the Fresnel interference can lead to apparent negative values of the film absorbance, with the extreme case being an apparent negative absorbance of $-0.44/\mu\text{m}$ for a film thickness of 0.02 μm . With a 2.5% film thickness nonuniformity, the Fresnel interference fringes are damped, and, for films thicknesses greater than 1 μm , the apparent absorbance values are all positive. Note, however, that the apparent values never match the true absorbance of the polymer film.

These results explain the large variability seen in the calculated absorbance values of the polymer films tested using transmission based absorbance measurements. Even given the variability, these relatively simple and quick measurements do give reasonable estimates of the absorbance of the material. For quantitative measurements, the effects of Fresnel interference and film thickness nonuniformity must be taken into consideration. This can be accomplished using VUV spectroscopy which includes analysis of both the reflectance and transmission measurements, or more directly using spectroscopic ellipsometry to model the film substrate system explicitly.

4. CONCLUSIONS

With the introduction of 157 nm as the next optical lithography wavelength, the need for new pellicle and photoresist materials optimized for this wavelength has produced much activity in optical characterization of thin film materials. Here we focus on ultratransparent fluoropolymers for 157 nm pellicle applications that require absorbances below 0.01/ μm to achieve transmissions above 98%.

Since 157 nm is in the vacuum ultraviolet (VUV), below the 190 nm air cutoff, vacuum or nitrogen purged optical systems are required. VUV spectrophotometers, using both traditional deuterium lamps or laser plasma light sources (LPLS), are being used for transmission based VUV absorbance measurements. These absorbance measurements, however, do not typically compensate for the index mismatch between substrate and film, the Fresnel interference fringes in the thin film or the effects of film thickness nonuniformity, nor do they help determine film thickness. Spectroscopic ellipsometry using polarized reflectance measurements offers the possibility of higher accuracy optical property determination, providing the technical demands of ellipsometry in the VUV can be met. The J. A. Woollam VUV-Vase ellipsometer is a monochromator-based instrument with an AutoRetarder for improved sensitivity and covers the spectral region from 142 to 1700 nm.

Comparison of VUV absorbance measurements of fluoropolymer thin films on CaF_2 substrates, with VUV ellipsometry measurements of the same polymers on silicon substrates, demonstrates some of the artifacts in, and helps define the accuracy of, transmission based absorbance measurements. The antireflective nature of these polymer films can increase the transmission of the film coated substrate, producing apparent negative absorbance values from VUV spectroscopy. In addition, Fresnel interference fringes can produce transmission oscillations that can lead to underestimation of the film absorbance. Film thickness nonuniformity can serve to reduce the Fresnel interference fringes, leading to reduced variation in the apparent 157 nm absorbance of μm thick films.

VUV ellipsometry coupled with Fresnel analysis of the thin film/substrate system formally takes into consideration all of these optical artifacts, while at the same time determining the complex index of refraction of the materials. The absorbance values do not show large apparent oscillations, the film thickness is directly determined in the measurement, and film microstructure can also be modeled. Similar Fresnel analysis can be applied to VUV spectroscopy measurements if both reflectance and transmission are measured and analyzed.

Transmission based absorbance/ μm measurements performed using VUV spectroscopy are characterized by rapid turn around time, and are essential during the materials design and screening phase of a new materials development program. Once suitable candidate materials families have been identified for development, VUV ellipsometry becomes essential so as to model the film structure, characterize the complex index of refraction, and design the pellicle film as a tuned etalon.

From these VUV spectroscopy and ellipsometry measurements, we have identified ultratransparent fluoropolymers that have 157 nm absorbances below 0.01/ μm . These materials have the appropriate optical properties for use as 157 nm pellicles with greater than 98% transmission. This is an important finding for 157 nm lithography, since the lack of an 157nm pellicle has been identified as a critical path issue.

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